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71 Applicant: THE PROCTER & GAMBLE COMPANY  
301 East Sixth Street  
Cincinnati Ohio 45201(US)

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71 Applicant: Procter & Gamble Limited  
Hedley House  
Gosforth Newcastle upon Tyne NE99 1EE(GB)

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GB

72 Inventor: Atkinson, Ronald Edward  
Broomely Osborne Avenue  
Hexham Northumberland(GB)

72 Inventor: Wilmshurst, Stephen James  
5204 Williamsburg Road, NW  
Cincinnati Ohio 45215(US)

72 Inventor: Lawson, John Russell  
15 The Foxhills Fellside Park  
Whickham Newcastle NE16 5UU(GB)

74 Representative: Gibson, Tony Nicholas et al,  
Procter & Gamble (NTC) Limited Whitley Road  
Longbenton Newcastle upon Tyne NE12 9TS(GB)

54 Liquid detergent compositions.

57 Stable liquid dishwashing compositions are provided incorporating an alkyl benzene sulphonate and/or alkyl sulphate, an alkyl ethoxy sulphate and an ethoxylated C<sub>8</sub>-C<sub>18</sub> alcohol containing an average of (E<sub>av</sub>) from 1.5 to 25 moles of ethylene oxide per mole of alcohol and wherein the ethoxylated alcohol contains no more than 1% by weight of unethoxylated alcohol when E<sub>av</sub><9 and no more than 2% by weight of unethoxylated alcohol when 9<E<sub>av</sub><25.

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## LIQUID DETERGENT COMPOSITIONS

R E Atkinson

S J Wilmshurst

J R Lawson

5     Field of the Invention

This invention relates to aqueous liquid detergent compositions and particularly to dishwashing compositions incorporating a mixture of anionic and ethoxylated nonionic surfactants.

10    Background of the Invention

Liquid detergent compositions intended for use as dishwashing products conventionally take the form of clear aqueous solutions containing a mixture of one or more sulphate and sulphonate anionic surfactants together with a suds stabilising agent. Where sulphonate surfactants are used in such mixtures they may be of the olefin sulphonate, paraffin sulphonate or most usually alkyl benzene sulphonate type whilst alkyl sulphates and alkyl ether sulphates form the sulphate species commonly employed. Recently there has been a trend towards the use of magnesium cations for at least part of the anionic surfactants present and the disclosures of British Patent Specifications Nos. 1,524,441 and 1,551,074, British published Patent Application No. 2,010,893 A and European Patent Application Publication No. 0039110 are representative of the state of the art. The art teaches that these formulations have enhanced performance, particularly when used in water of low mineral hardness. Nevertheless, the pressure to improve the cost-effectiveness

of liquid detergent compositions has meant that the search has continued for compositions having improved economy, performance and in-use characteristics. In particular, intensive effort has been expended in increasing the concentration of dishwashing liquid detergent compositions and in reducing the level of diluents such as water and solubilising hydrotropes without sacrificing the storage stability of the compositions.

In most liquid dishwashing detergent compositions based primarily on anionic surfactants the use of anionic surfactant levels above about 30% by weight of the composition (the precise value being dependent on the surfactants employed) demands an increase in hydrotrope level. An exception to this general pattern of behaviour is, however, provided by paraffin sulphonates, commercial sources of which contain disulphonate components which are believed to provide some hydrotrope characteristics. These components make compositions containing paraffin sulphonates more tolerant towards otherwise poorly soluble ingredients such as inorganic salts and certain suds stabilisers such as alkanolamides. Exemplary disclosures of such compositions are provided by British Patent Nos. 1451228, 1567421 and 1382295. In the absence of a significant level (e.g. 5%) of paraffin sulphonates, the addition of suds stabilisers such as alkanolamides and amine oxides requires additional hydrotrope in order to maintain the phase stability of the composition on storage.

Ethoxylated nonionic surfactants constitute a class of materials capable of solubilising other components in aqueous media but this capability is strongly dependent on their average degree of ethoxylation ( $E_{av}$ ). Highly ethoxylated nonionic surfactants, (i.e.  $E_{av} > 20$ ), are very hydrophilic in nature and thus tend to reduce the oily soil removal capability of liquid dishwashing detergent formulations, which is undesirable where oil and grease removal is an important criterion of consumer acceptance. Highly

ethoxylated nonionics having hydrocarbon chain lengths less than  $C_{12}$  are not readily available commercially, but longer chain length materials having high levels of ethoxylation which are available in bulk (e.g. tallow alcohol ethoxylates) tend to have  
5 suds suppressing characteristics and also tend to be relatively poor oil and grease removal agents. On the other hand, nonionic surfactants having low levels of ethoxylation (i.e.  $E_{av} < 2$ ) are relatively hydrophobic and have a limited ability to solubilise other components in the absence of other surfactant species..

10 A feature shared by all ethoxylated nonionic surfactants is the presence of a level of unethoxylated material, the magnitude of which depends on the degree of ethoxylation, but which can constitute up to 20% by weight of the nonionic surfactant. Unethoxylated  $C_6$ - $C_{13}$  aliphatic primary alcohols are odorous  
15 materials having a low water solubility, and these characteristics are discernible in the ethoxylated alcohols to an extent which depends on the level of ethoxylation, the effect diminishing as  $E_{av}$  increases. The comparatively low level of usage of ethoxylated alcohol surfactants in particulate laundry  
20 detergent formulations makes the odour characteristics of the ethoxylated alcohol of relatively minor importance in such products, particularly granular products for use in automatic washing machines. However, consumers tend to be very aware of the physical characteristics of liquid detergent compositions,  
25 particularly those used for dishwashing, because of the manual nature of the task and the greater degree of exposure of the consumer to the hot wash liquor. Dishwashing liquid detergent formulations are commercially available containing paraffin sulphate as the principal anionic species together with  
30 ethoxylated nonionic surfactants having  $E_{av}$  in the range 2-6 so that such formulations have a measure of aesthetic acceptance by consumers. However, for surfactant mixtures not containing paraffin sulphate, the adverse influence of unethoxylated components in the nonionic surfactant on the phase stability  
35 characteristics of liquid dishwashing detergents has been judged to be unacceptable.

In particular, liquid dishwashing detergent compositions containing alkyl sulphates and/or alkyl benzene sulphonates have been found to be subject to odour and storage stability problems when formulated with ethoxylated nonionic surfactants containing the normal spread of ethoxylated species, and this effect is more pronounced when the composition also contains magnesium ions. However, it has now been found that certain alcohol ethoxylates, containing less than a defined amount of unethoxylated species, and from which preferable at least part of the mono-ethoxylated species has been removed, can be incorporated in alkyl benzene sulphonate- or alkyl sulphate-containing liquid dishwashing compositions without adverse effect on the storage stability of the latter.

#### Summary of the Invention

According to the present invention therefore there is provided a physically stable liquid detergent composition comprising from 20-85% of an anionic surfactant system consisting essentially of a  $C_{10}-C_{16}$  alkyl benzene sulphonate salt and/or a  $C_{10}-C_{16}$  primary alkyl sulphate salt together with a  $C_{10}-C_{16}$  primary alkyl ethoxy sulphate salt containing an average of not more than 6 ethylene oxide groups per alkyl group in the alkyl ether sulphate, and optionally including a suds stabilising agent wherein the composition also includes from 1-10% of an ethoxylated  $C_6-C_{13}$  aliphatic alcohol containing an average of from 1.5 to 25 moles of ethylene oxide per mole of alcohol, said ethoxylated alcohol containing not more than 1% by weight of unethoxylated alcohol where the ethoxylated alcohol contains an average of less than 9 moles of ethylene oxide and not more than 2% by weight of unethoxylated alcohol where the ethoxylated alcohol contains an average of from 9 to 25 moles of ethylene oxide per mole of alcohol.

Preferably the ethoxylated aliphatic alcohol has an HLB in the range from 8.0 to 17.0 more preferably from 11.0 to 17.0, and most preferably from 11.0 to 15.0.

In preferred compositions in accordance with the invention the ethoxylated aliphatic alcohol is a  $C_9-C_{11}$  primary alcohol condensed with an average of from 6 to 10

- moles of ethylene oxide per mole of alcohol. Preferably the ethoxylated alcohol contains less than 0.7%, most preferably less than 0.5% of unethoxylated material, and in highly preferred compositions the level of mono-ethoxylated
- 5  $C_9-C_{11}$  alcohol is no more than 5% by weight of the nonionic surfactant.

- Preferred liquid detergent compositions, in accordance with the invention, incorporate an alkyl sulphate surfactant and magnesium ions in a molar amount corresponding to at
- 10 least half of the molar amount of the alkyl sulphate present and contain from 1% to 5% by weight of the ethoxylated alcohol.

- One preferred group of compositions incorporates a three component anionic surfactant system, comprising 8-12% by
- 15 weight of the composition of  $C_{10}-C_{16}$  primary alkyl sulphate, 9-11% of a  $C_{10}-C_{16}$  primary alkyl ethoxysulphate containing an average of from 1.5 to 3 ethoxy groups per alkyl group, and 13-17% of a  $C_{10}-C_{16}$  alkyl benzene sulphonate. The cations in this system are a mixture of
- 20 ammonium and magnesium ions, the level of magnesium corresponding to approximately one half of the molar amount of alkyl sulphate present.

- Another preferred group of compositions employs a two component anionic surfactant system comprising from 4-8%
- 25  $C_{10}-C_{16}$  primary alkyl sulphate and from 20-25%  $C_{10}-C_{16}$  alkyl ethoxy sulphate containing from 0.5 to 2.0 ethoxy groups per alkyl group.

- Preferably compositions in accordance with the invention also contain 2%-8%, most preferably 3%-4% by weight of a suds
- 30 booster selected from  $C_{10}-C_{16}$  mono and di  $C_2-C_3$  alkanolamides, and  $C_8-C_{18}$  alkyl di  $C_1-C_3$  alkyl amine oxides.

Description of the Invention

Detergent compositions in accordance with the present invention comprise a mixture of anionic surfactants of defined constitution, an amount of from 20% to 50% by weight of the composition, together with an ethoxylated nonionic surfactant having a low content of unethoxylated material.

All compositions in accordance with the invention incorporate an alkyl sulphate and/or an alkyl benzene sulphonate component in combination with an alkyl ethoxy sulphate.

The alkyl sulphate component is a primary alkyl sulphate in which the alkyl group contains 10-16 carbon atoms, more preferably an average of 12-14 carbon atoms. The alkyl group may be linear or branched in configuration.

C<sub>10</sub>-C<sub>16</sub> alcohols, derived from natural fats or Ziegler olefin build-up or OXO synthesis, form suitable sources for the alkyl group. Examples of synthetically derived materials include Dobanol 23 (RTM) sold by Shell Chemicals (UK) Ltd, Ethyl 24 sold by the Ethyl Corporation, a blend of C<sub>13</sub>-C<sub>15</sub> alcohols in the ratio 67% C<sub>13</sub>, 33% C<sub>15</sub> sold under the trade name Lutensol by BASF GmbH and Synperonic (RTM) by ICI Ltd, and Lial 125 sold by Liquichimica Italiana. Examples of naturally occurring materials from which the alcohols can be derived are coconut oil and palm kernel oil and the corresponding fatty acids.

When present in compositions in accordance with the invention, the level of the alkyl sulphate component lies in the range of from 4% to 20% by weight of the composition, more generally from 4% to 16% by weight. In one preferred compositional aspect of the invention in which alkyl benzene sulphonate is also incorporated, the usage level lies in the range from 8% to 12% by weight, most preferably in the range from 8% to 11% by weight. In another compositional aspect of the invention in which a sulphonate component is not present, the alkyl sulphate level lies in the range from 12% to 20%, more preferably from 14% to 18% by weight.

For the purposes of the present invention any alkali metal, alkali earth metal, ammonium or substituted ammonium cation can be used in association with the alkyl sulphate. However, in highly preferred compositions in accordance with the invention the alkyl sulphate is associated with a source of magnesium ions which, as will be described hereinafter, can either be introduced as the oxide or hydroxide to neutralise the acid, or can be added to the composition as a water soluble salt. The addition of appreciable levels of magnesium salts to the dishwashing compositions of the invention raises the temperature at which inorganic salt crystals form in the compositions on cooling and is therefore less preferable.

In compositions comprising a mixture of alkyl benzene sulphonate, alkyl sulphate and alkyl ether sulphate, the molar amount of magnesium ion in the compositions is controlled to correspond to 0.20-0.70X, preferably 0.45-0.55X where X is the number of moles of  $C_{10}$ - $C_{16}$  alkyl sulphate present. Most preferably the magnesium ion content is adjusted to provide the stoichiometric equivalent of the alkyl sulphate present. In practice the magnesium ion will be present at a level of from about 0.15% to about 0.70% by weight, preferably from 0.25% to 0.55% by weight of the composition.

By contrast, compositions containing only alkyl sulphate and alkyl ether sulphate as the anionic surfactants will preferably contain up to about 0.90% by weight of the composition of magnesium ion, and part of the alkyl ether sulphate will also be neutralised by magnesium ion.

Alkyl benzene sulphonates useful in compositions of the present invention are those in which the alkyl group, which is substantially linear, contains 10-16 carbon atoms, preferably 11-13 carbon atoms, a material with an average carbon chain length of 11.8 being most preferred. The phenyl isomer distribution, i.e. the point of attachment of the

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alkyl chain to the benzene nucleus, is not critical but alkyl benzenes having a high 2-phenyl isomer content are preferred. When employed in compositions in accordance with the present invention, an alkylbenzene sulphonate content of  
5 from 10% to 28% by weight of the composition is required generally from 12% to 26% by weight. In a preferred aspect of the invention an alkylbenzene sulphonate content of from 13% to 17% by weight is used and highly preferred compositions in accordance with this aspect of the invention  
10 have from 14% to 17% of  $C_{11.8}$  alkyl benzene sulphonate.

The alkyl ethoxy sulphate surfactant component comprises a primary alkyl ethoxy sulphate derived from the condensation product of a  $C_{10}$ - $C_{16}$  alcohol with an average of up to 6 ethylene oxide groups. The  $C_{10}$ - $C_{16}$  alcohol itself can be  
15 obtained from any of the sources previously described for the alkyl sulphate component. It has, however, been found preferable to use alkyl sulphate and alkyl ether sulphate in which the carbon chain length distributions are the same.  $C_{12}$ - $C_{13}$  alkyl ether sulphates are preferred and the level  
20 of alkyl ethoxy sulphate in the composition lies between 8% and 25% by weight of the compositions, generally in the range from 10% to 25% by weight. In the preferred aspect of the invention incorporating an alkyl benzene sulphonate surfactant, the level lies in the range from 9% to 15% by  
25 weight, most preferably in the range from 9% to 11% by weight.

Conventional ethoxylation processes result in a distribution of individual ethoxylates ranging from 1 to 10 ethoxy groups per mole of alcohol, so that the desired average can be obtained in a variety of ways. Blends can be  
30 made of material having different degrees of ethoxylation and/or different ethoxylate distributions arising from the specific ethoxylation techniques employed and subsequent processing steps such as distillation. For example, it has been found that equivalent sudsing and grease removal  
35 performance to that given by a blend of alkyl sulphate and

alkyl triethoxy ether sulphate can be obtained by reducing the level of alkyl sulphate and using an alkyl ether sulphate with an average of approximately two ethoxy groups per mole of alcohol. In preferred compositions in accordance with the present invention the average degree of ethoxylation is from 0.5 to 4, more preferably from 0.8 to 2.0.

The counter ion for the alkyl ethoxy sulphate can be any one of sodium, potassium, ammonium or alkanol-ammonium or a mixture thereof. However, for the purposes of obtaining the lowest possible chill point temperature, (the temperature at which inorganic salt crystals separate), it is desirable that at least 30% of the counter ions for the alkyl ethoxy sulphate should be ammonium. In compositions containing an alkyl benzene sulphonate component it is highly preferred that the alkyl ethoxy sulphate is completely neutralized by ammonium ions.

The counter ions in association with the alkyl benzene sulphonate are independently selected in the same manner as those for the alkyl ethoxy sulphate, there being preferably at least 50% of ammonium ions. In order for compositions in accordance with the invention to have a chill point of 0°C, at least 70% of the neutralising cations for the anionic surfactants should be ammonium ions and most preferably ammonium constitutes the only cation present other than magnesium.

The ethoxylated nonionic surfactant component of the invention is a  $C_6-C_{13}$  aliphatic alcohol ethoxylate containing an average of from 1.5 to 25, more preferably from 2 to 15 and most preferably from 6 to 10 moles of ethylene oxide per mole of alcohol. The aliphatic alcohol ethoxylate contains not more than 1% by weight of unethoxylated alcohol where the ethoxylated alcohol contains an average of less than 9 moles of ethylene oxide and not more than 2% by weight of unethoxylated alcohol where the ethoxylated alcohol contains an average of from 9 to 25 moles of ethylene oxide per mole of alcohol.

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The starting alcohol may be a primary or secondary alcohol but is preferably a primary alcohol which may be derived from natural or synthetic sources. Thus natural fats or oils, or products of Ziegler olefin build up reactions or OXO synthesis may all be used as the source of the hydrocarbon chain, the structure of which may be linear or branched in type.

The preferred alcohol chain length range is from  $C_9$ - $C_{11}$  as it has been found that performance, viz. sudsing volume and mileage, are optimum for ethoxylates made from such alcohols.

The average degree of ethoxylation ( $E_{av}$ ) lies in the range from 1.5 to 25 moles per mole of alcohol, but is preferably in the range from 2-15 and most preferably in the range from 6 to 10 moles per mole of alcohol. It is also desirable for performance reasons that the hydrophilic-lipophilic balance (HLB) of the ethoxylated alcohol is in the range from 8.0 to 17.0, more preferably from 11.0 to 17.0 and most preferably from 11.0 to 15.0.

As discussed with respect to the alkyl ethoxy sulphate component, a normal (base catalysed) ethoxylation process results in a wide distribution of ethoxylate species. For an average degree of ethoxylation of from 6 to 10 moles per mole of alcohol, this range extends from 1 to at least 15 moles of ethylene oxide per mole of alcohol and for an average in the range of from 20 to 25 moles per mole of alcohol the range may extend up to 50 moles/mole of alcohol. Increases in  $E_{av}$  cause the ethoxylate distribution to become less peaked about the average value and also lead to a reduction in the level of unethoxylated material. Condensation products having an  $E_{av}$  in the range from 3 to 9 moles per mole of alcohol contain 3-20% unethoxylated material while products having an  $E_{av}$  in the range from 10 to 20 moles per mole of alcohol will still contain up to 2% of unethoxylated material.

In the liquid dishwashing detergent compositions of the invention, levels of unethoxylated material in the ethoxylated nonionic surfactant of greater than 2% by weight will give rise to phase stability/chill point problems and/or will result in a product having a fatty alcohol odour which is

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unacceptable to consumers and which is difficult to mask with conventional detergent perfumes. It has been found that for phase stability reasons the maximum level of unethoxylated alcohol that can be tolerated in the ethoxylated alcohol component is 1% by weight of the alcohol ethoxylate where the level of ethoxylation is less than 9 moles per mole of alcohol and 2% by weight where the level of ethoxylation is from 9 to 25 moles per mole of alcohol. More preferably the unethoxylated alcohol level is not more than 0.7% and most preferably is less than 0.5% by weight of the ethoxylated alcohol component.

Distillation under vacuum is employed to remove the undesired material and this also removes a portion of the monoethoxylate fraction, thereby increasing the  $E_{av}$  of the remaining material. In preferred embodiments of the invention in which the ethoxylated alcohol is a  $C_9-C_{11}$  primary alcohol ethoxylate the level of monoethoxylate is not more than 5% by weight of the ethoxylated alcohol.

The level of usage of the ethoxylated alcohol component in compositions of the invention is from 1 to 10% by weight, more preferably from 1 to 5% and most preferably from 2% to 4% by weight. Liquid dishwashing detergent compositions in accordance with the invention, and incorporating from 3% to 5% by weight of a primary alcohol containing from 9 to 11 carbon atoms condensed with an average of from 5 to 10 moles ethylene oxide per mole of alcohol to give an HLB value in the range of from 12 to 15, the alcohol ethoxylate containing <0.5% by weight of unethoxylated alcohol, display chill points <0°C together with enhanced sudsing and mileage performance relative to prior art compositions.

A highly preferred ingredient of the composition according to the invention is a suds-promoting agent present at a level of from 2% to 8% by weight of the composition, preferably from 3% to 6% and most preferably 3%-4%.

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The suds-promoting agent can be any of  $C_{10}$ - $C_{16}$  mono- and di- $C_2$ - $C_3$  alkanolamide, and tertiary amine oxides containing a  $C_8$ - $C_{18}$  alkyl group.

Examples of the alkanolamides are coconut alkyl  
5 monoethanolamide, coconut alkyl diethanolamides and palm  
kernel and coconut alkyl mono and di isopropanol amides. The  
palm kernel or coconut alkyl residue may either be 'whole  
cut', including the  $C_{10}$  and  $C_{16}$  fractions or may be the  
so-called 'narrow-cut'  $C_{12}$ - $C_{14}$  fraction. Synthetic  
10 sources of the  $C_{10}$ - $C_{16}$  alkyl group can also be used.

Amine oxides useful in the present invention have one  
alkyl or hydroxyalkyl moiety of 8 to 18 carbon atoms,  
preferably 8 to 16 carbon atoms and two moieties selected  
from alkyl groups and hydroxyalkyl groups containing 1 to 3  
15 carbon atoms. Examples of such materials include  
dimethyloctylamine oxide, diethyldecylamine oxide,  
bis-(2-hydroxyethyl) dodecylamine oxide, methylethylhexa-  
decylamine oxide, and dimethyl-2-hydroxyoctadecylamine oxide.

A highly preferred example of the tertiary amine oxide is  
20 a  $C_{12}$ - $C_{14}$  alkyl dimethyl amine oxide in which the  
 $C_{12}$ - $C_{14}$  alkyl group is derived from coconut oil.

The balance of the formula comprises a hydrotrope-water  
system in which the hydrotrope may be urea, a  $C_1$ - $C_3$   
aliphatic alcohol, or a lower alkyl benzene sulphonate or  
25 mixtures of any of these. Normally a single hydrotrope will  
be adequate to provide the required phase stability, but  
compositions in accordance with the present invention  
preferably employ a mixture such as urea-alcohol-water or  
alcohol-lower alkyl benzene sulphonate-water in order to  
30 achieve the desired viscosity, and to remain stable and  
easily pourable. For compositions having an organic active  
concentration less than about 40% by weight, the preferred  
alcoholic hydrotrope is ethanol which is employed at from 3%  
to 10% by weight of the composition, preferably at from 4% to  
35 8%, usually in admixture with urea. Mixtures of hydrotropes

can, of course, be employed for cost effectiveness reasons irrespective of any stability/viscosity considerations.

Optional ingredients of the liquid detergent compositions of the invention include opacifiers such as ethylene glycol distearate, antibacterial agents such as glutaraldehyde and Bronopol (RIM), antitarnish agents such as benzoxymazole, heavy metal chelating agents such as EDTA or ETDMP, perfumes and dyes. The pH of the compositions may be anywhere within the range 6-7.5 but as manufactured the compositions normally have a pH in the range 6.6-7.3 and are subjected to a final pH trimming operation to obtain the desired finished product pH. For coloured products the pH preferably lies in the range 6.6-6.9 in order to maintain colour stability.

The compositions of the invention can be made in a number of ways but it is preferred that the ethoxylated nonionic surfactant is incorporated towards the end of the making process if not actually forming the last ingredient to be added. This is particularly important where the ethoxylated nonionic surfactant has an HLB 9.5 which is normally taken to be the value below which such materials are basically water insoluble.

Thus, individual anionic surfactants can be made as aqueous solutions of alkali metal or ammonium salts which are then mixed together with the suds booster and with the hydrotrope, following which any magnesium ion can be introduced as a water soluble salt such as the chloride or sulphate. The ethoxylated nonionic surfactant and any optional minor ingredients are then added at the same time as the pH and viscosity are adjusted. This method has the advantage of utilising conventional techniques and equipment but does result in the introduction of additional chloride or sulphate ions which can increase the chill point temperature (the temperature at which inorganic salts precipitate as crystals in the liquid).

An alternative and preferred method is to mix an alcohol and alcohol ethoxylate together and carry out a single sulphation and neutralisation. For this, the alcohol and alcohol ethoxylate should be mixed in a weight ratio lying in the range 4:3 to 1:6. Sulphation can take place by means of any of the conventional sulphating agents such as e.g. sulphur trioxide or chlorosulphonic acid. Neutralisation of the alkyl ether sulphuric acid and the alkyl sulphuric acid is carried out with the appropriate alkali or with a magnesium oxide or hydroxide slurry which avoids the addition of chloride or sulphate ions. In preferred executions of this technique in which magnesium hydroxide slurry is employed, it is convenient to use a mixture of these acids, as the magnesium salt of the alkyl ether sulphuric acid has relatively greater aqueous solubility than the alkyl sulphuric acid component. The suds booster is then dissolved in this heel of alkyl sulphate and alkyl ether sulphate actives.

The separately neutralised alkyl benzene sulphonate salt, and the neutralised alkyl and alkyl ether sulphate salts containing the suds booster and hydrotrope are then added to the final mixing tank and the ethoxylated nonionic surfactant and any optional ingredients added before the pH is adjusted as above.

Preferred compositions in accordance with the invention are clear single phase liquids, but the invention also embraces opaque products containing dispersed phases provided that such products are physically stable (i.e., do not separate) on storage.

The invention is illustrated in the following non-limitative examples in which all parts and percentages are by weight unless otherwise specified.

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EXAMPLE 1

The following compositions were prepared:

	A	B	C	D	E
5	Ammonium C <sub>11.8</sub> linear alkyl benzene sulphonate				
	14.2	14.2	14.2	14.2	14.2
	Ammonium C <sub>12-13</sub> alkyl (EO) <sub>2</sub> sulphate				
	10.4	10.4	10.4	10.4	10.4
	Magnesium C <sub>12-C13</sub> alkyl sulphate				
	8.6	8.6	8.6	8.6	8.6
10	Primary Alcohol ethoxylate				
	-	3.5 <sup>1</sup>	3.5 <sup>2</sup>	3.5 <sup>3</sup>	3.5 <sup>4</sup>
	Coconut Monoethanolamide				
	4.0	4.0	4.0	4.0	4.0
	Ethanol				
	9.1	9.1	9.1	9.1	9.1
	Water				
	_____ to 100 _____				
1	Dobanol (RIM) 91E <sub>5</sub>				
15	A predominantly linear C <sub>9-C11</sub> alcohol blend containing an average of 5 ethylene oxide units per mole of alcohol, supplied by Shell International Ltd and 'topped' to reduce the level of unethoxylated C <sub>9-C11</sub> alcohol to 0.5% by weight of the ethoxylate, thereby				
20	increasing the average degree of ethoxylation to approximately 6.				
2	Dobanol (RIM) 91E <sub>2.5</sub>				
25	A predominantly linear C <sub>9-C11</sub> alcohol blend containing an average of 2.5 ethylene oxide units per mole of alcohol.				
3	Dobanol (RIM) 23E <sub>6.5</sub>				
	A predominantly linear C <sub>12-C13</sub> alcohol blend containing an average of 6.5 ethylene oxide units per mole of alcohol.				

4 Dobanol (RTM) 45E<sub>7</sub>  
A predominantly linear C<sub>14</sub>-C<sub>15</sub> alcohol blend  
containing an average of 7 ethylene oxide units per mole  
of alcohol.

5 In the preparation of Composition A, a mixture of alcohol  
and alcohol ethoxylate was sulphated using SO<sub>3</sub>-air  
sulphation, and was then neutralised in an alcoholic ammonium  
hydroxide solution to which magnesium hydroxide had been  
added in an amount corresponding to half the molar quantity  
10 of alkyl sulphate present. A separate sulphonation of the  
alkyl benzene was employed to produce alkyl benzene sulphonic  
acid which was added to the alkaline solution of the other  
actives and neutralised with the excess ammonia to pH 7. The  
monoethanolamide was then added before final pH trimming to  
15 pH 6.8. The chill point of Composition A was -5°C.  
Compositions B-E were prepared in a similar manner except  
that the ethoxylated nonionic surfactant was added during the  
final pH trimming operation.

The chill point of the various compositions was measured  
20 and each composition was assessed for solution odour. A  
comparison of the suds mileage of the compositions under  
identical test conditions was also made using the mechanical  
sudsing test method described below under the following test  
conditions.

25 Product Concentration 0.12%

Water Temperature 47°C

Water Hardness 2°H and 18°H

Soil : Cake Mix / Mixed free fatty acids (MFFA)

The Cake Mix is McDougall's Sponge Mix

30 The free fatty acids comprise 2 parts oleic acid  
2 parts linoleic acid  
1 part stearic acid  
2.5 parts palmitic acid  
367 parts corn oil

35 to give 2% MFFA mixture.

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The method uses 4 cylinders of length 30 cm and diameter 10 cm fixed side by side, and rotatable at a speed of 24 rpm about a central axis. Each cylinder is charged with 500 mls of product solution at a concentration of 0.12% and a  
 5 temperature of 45°C. The outer two cylinders are used for one of the products being compared and the inner two for the other product.

The cylinders are rotated for 2 minutes, stopped, the initial suds are measured and a soil load is then added. The  
 10 grease soil comprises a mixture of fatty acids in a cooking oil base and 1 ml of this mixture (MFFA) is added to each cylinder. All of the particulate soil is also added at this stage. After 1 minute the cylinders are restarted and allowed to rotate for 1 minute. The suds height is noted and  
 15 1 ml of the 2% MFFA is added to each cylinder. After 1 minute the cylinders are restarted. This process continues until the suds height in the cylinder is lower than 0.5 cms.

Product A is designated as the control and suds mileage figures are calculated for the other product versus the  
 20 'control' product on the following basis.

Mileage of test product

= 
$$\frac{\text{number of soil additions to test product solution to reduce suds height to 0.5 cm}}{\text{number of soil additions to control product to reduce suds height to 0.5 cm}} \times 100$$
  
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The results of the chill point measurements and odour assessments and the mileage comparisons using Composition A as 100% were as follows:

5	Composition	Mileage		Chill Point °C	Odour Type
		2°H	18°H		
	B	114	120	-5	Bland
	C	113	100	+24	Strong fatty alcohol note
10	D	100	100	-1.5	Fatty alcohol note
	E	91	80	-4	Fatty alcohol note

15 It can be seen that only Composition B showed the combination of a consistent mileage advantage in both hard and soft water, an acceptable chill point and an acceptable odour.

#### EXAMPLE 2

The following compositions are in accordance with the present invention.

		F	G
20	Magnesium C <sub>12</sub> -C <sub>13</sub> alkyl sulphate	15.1	5.0
	Magnesium C <sub>12</sub> -C <sub>13</sub> alkyl (EO) <sub>1</sub> sulphate	-	15.1
	Magnesium C <sub>12</sub> -C <sub>13</sub> alkyl (EO) <sub>2</sub> sulphate	3.4	-
	Ammonium C <sub>12</sub> -C <sub>13</sub> alkyl (EO) <sub>1</sub> sulphate	-	8.1
	Ammonium C <sub>12</sub> -C <sub>13</sub> alkyl (EO) <sub>2</sub> sulphate	9.7	-
25	C <sub>9</sub> -C <sub>11</sub> primary linear alcohol (EO) <sub>6</sub> containing < 1% unethoxylated alcohol	3.5	3.5

	C <sub>12</sub> monoethanolamide	4.0	-
	C <sub>12</sub> -C <sub>13</sub> alkyl dimethyl amine oxide	-	2.7
	Ethanol	8.5	5.0
	Urea	-	-
5	Sodium xylene sulphonate	-	3.0
	Water	—to 100 —	

### EXAMPLE 3

Compositions were made up in accordance with Example 1 except that the type, level\* and HLB of ethoxylated primary alcohol surfactant was as follows

	Nonionic Type	Level	HLB
	H Commercial C <sub>10</sub> alcohol (EO) <sub>10</sub>	4.95%	14.7
	I Commercial C <sub>9</sub> -C <sub>11</sub> alcohol (EO) <sub>5</sub> (topped to remove an ethoxylated species to give an (EO) value of 6.5)	3.5	12.5
15	J C <sub>8</sub> (EO) <sub>4.8</sub>	2.7	12.4
	K C <sub>6</sub> -C <sub>8</sub> -C <sub>10</sub> alcohol blend (EO) <sub>5</sub>	3.5	12.2
	L C <sub>10</sub> (EO) <sub>20</sub>	8.7	16.9
	M C <sub>6</sub> (EO) <sub>1.5</sub>	1.45	8.3
20	N C <sub>6</sub> (EO) <sub>3.5</sub>	2.11	12.0
	O C <sub>8</sub> (EO) <sub>2</sub>	1.90	8.7
	A A reference composition, nil nonionic surfactant		

\*Levels were adjusted to provide the same molar quantity as in Composition I.

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The suds mileage of the above compositions was compared using the procedure of Example 1 to give the following results

		H	I	J	K	L	M	N	O	A
5	Particulate	°S	130	120	119	119	102	109	109	100
	Soil	°H	113	114	112	112	100	133	133	100
	Greasy	°S	130	122	107	106	75	110	120	100
	Soil	°H	116	112	103	106	117	114	108	100

10 All of the Compositions H-O inclusive show advantages over the Comparison Composition A which does not contain an ethoxylated nonionic component. It can also be seen that Compositions H & I which represent preferred embodiments of the invention provide superior performance to other, less preferred, embodiments such as Compositions L & M.

CLAIMS

1. A physically stable liquid detergent composition comprising from 20-80% of an anionic surfactant system consisting essentially of a C<sub>10</sub>-C<sub>16</sub> alkyl benzene sulphate salt and/or a C<sub>10</sub>-C<sub>16</sub> primary alkyl sulphate salt together with a C<sub>10</sub>-C<sub>16</sub> primary alkyl ethoxy sulphate salt containing an average of not more than 6 ethylene oxide groups per alkyl group in the alkyl ether sulphate, and optionally including a suds stabilising agent characterised in that the composition also includes from 1-10% of an ethoxylated C<sub>6</sub>-C<sub>13</sub> aliphatic alcohol containing an average of from 1.5 to 25 moles of ethylene oxide per mole of alcohol, said ethoxylated alcohol containing not more than 1% by weight of unethoxylated alcohol where the ethoxylated alcohol contains an average of less than 9 moles of ethylene oxide and not more than 2% by weight of unethoxylated alcohol where the ethoxylated alcohol contains an average of from 9 to 25 moles of ethylene oxide per mole of alcohol.
2. A liquid detergent composition according to claim 1 characterised in that the ethoxylated aliphatic alcohol has an HLB in the range from 8.0 to 17.0.
3. A liquid detergent composition according to either one of claims 1 or 2 wherein the ethoxylated aliphatic alcohol contains an average of from 6 to 10 moles of ethylene oxide per mole of alcohol.
4. A liquid detergent composition according to any one of claims 1-3 wherein the ethoxylated aliphatic alcohol has an HLB in the range from 11.0 to 17.0 preferably from 11.0 to 15.0.

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5. A liquid detergent composition according to any one of claims 1-4 wherein the alcohol ethoxylate contains less than 0.7%, preferably less than 0.5% by weight of unethoxylated alcohol.
- 5 6. A liquid detergent composition according to any one of claims 1-5 wherein the alcohol ethoxylate is a primary alcohol ethoxylate.
7. A liquid detergent composition according to any one of claims 1-6 wherein the aliphatic alcohol has an alkyl chain  
10 length of from 9 to 11 carbon atoms.
8. A liquid detergent composition according to any one of claims 1-7 wherein the ethoxylated nonionic surfactant contains an average of less than 9 moles of ethylene oxide per mole of alcohol and the level of monoethoxylated alcohol  
15 in the alcohol ethoxylate is no more than 5% by weight of the alcohol ethoxylate.

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**EUROPEAN PATENT APPLICATION**

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㉑ Applicant: **THE PROCTER & GAMBLE COMPANY**  
301 East Sixth Street  
Cincinnati Ohio 45201(US)

㉕ Designated Contracting States:  
BE CH DE FR IT LI NL SE AT

㉑ Applicant: **Procter & Gamble Limited**  
Hedley House  
Gosforth Newcastle upon Tyne NE99 1EE(GB)

㉕ Designated Contracting States:  
GB

㉒ Inventor: **Atkinson, Ronald Edward**  
Broomely Osborne Avenue  
Hexham Northumberland(GB)

㉒ Inventor: **Wilmshurst, Stephen James**  
5204 Williamsburg Road, NW  
Cincinnati Ohio 45215(US)

㉒ Inventor: **Lawson, John Russell**  
15 The Foxhills Fellside Park  
Whickham Newcastle NE16 5UU(GB)

㉒ Representative: **Gibson, Tony Nicholas et al,**  
**Procter & Gamble (NTC) Limited** Whitley Road  
Longbenton Newcastle upon Tyne NE12 9TS(GB)

㉕ Liquid detergent compositions.

㉕ Stable liquid dishwashing detergent compositions are provided incorporating an alkyl benzene sulphonate and/or alkyl sulphate, an alkyl ethoxy sulphate and an ethoxylated C<sub>8</sub>-C<sub>13</sub> alcohol containing an average of (E<sub>av</sub>) from 1.5 to 25 moles of ethylene oxide per mole of alcohol and wherein the ethoxylated alcohol contains no more than 1% by weight of unethoxylated alcohol when E<sub>av</sub> < 9 and no more than 2% by weight of unethoxylated alcohol when 9 < E<sub>av</sub> < 25.

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## EUROPEAN SEARCH REPORT

Application number

EP 84 30 3044

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
Y	DE-B-2 945 301 (A. OPEL) * Whole document *	1-8	C 11 D 1/83 C 11 D 1/22 C 11 D 1/14 C 11 D 1/29
Y	--- CHEMICAL ABSTRACTS, vol. 88, no. 4, 23th January 1978, page 80, abstract no. 244530r, Columbus, Ohio, US; & JP-A-77 82 909 (DASUKIN FRANCHISE CO., LTD.) 11-07-1977	1-8	C 11 D 1/72 C 11 D 17/00
Y	--- CHEMICAL ABSTRACTS, vol. 80, no. 14, 8th April 1974, page 48, abstract no. 72322f, Columbus, Ohio, US; & JP-A-73 73 409 (KAO SOAP CO., LTD.) 03-10-1973	1-8	
Y	--- CHEMICAL ABSTRACTS, vol. 93, no. 22, 1980, page 110, abstracts no. 206525d, Columbus, Ohio, US; & JP-A-80 86 894 (KAO SOAP CO., LTD.) 01-07-1980	1-5	TECHNICAL FIELDS SEARCHED (Int. Cl. 4)  C 11 D
P,X	--- EP-A-O 102 124 (UNILEVER) * Whole document *	1-8	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 23-04-1987	Examiner GOLLER P.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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